

Cu (II)-Red Onion Skin Extract-Azo metal Complex - A Potential for Oilfield Applications

ABSTRACT

Red Onion skin extract (ROSE)- azo compound of 2-aminophenol and Cu (II) metal complex of the azo compound (Cu-APmROSE) were formed and characterized using FT-IR spectroscopy, UV-Visible absorption spectroscopy and Scanning electron microscopy. The IR Spectra showed the values of N=N-stretching frequency of 1512.24cm^{-1} at 1500cm^{-1} in APmROSE. This stretching frequency is absent in the Cu-APmROSE. This is an indication of the involvement of the N=N- bond in coordination to the metal. APmROSE shows an absorption maximum at 512 nm. This band was shifted to 334 nm in Cu-APmROSE. This suggests an interaction between the Cu and the azo compound.

(Key words: 2-aminophenol, red onion skin extract, Cu-APmROSE, Complex, diazotization.)

1.0 INTRODUCTION

Onion is amongst the crops highly cultivated in the world today, probably because they have long storage time and they are easy to transport (Chu, Kang, & Wang, 2017). *Allium cepa* is believed to have emanated from central Asia; they are contained in the Liliaceae and wild species and are spread across Europe, Asia, North America and Africa. They are attuned to temperate environments with low or fluctuating supplies of water and are biennial (Akaranta & Akaho, 2012; Griffiths *et al*, 2002). Onion is used to improve the taste of other foods due to its flavour and pungency resulting from its sulphur content (Bello *et al*, 2013). It has been extensively used from time immemorial in many parts of the Earth as vegetables and medicine and has a number of medicinal values, including antioxidant, antithrombotic, antiasthmatic and antibiotic effects and it is known to be rich in flavonoids (Ifesan, 2017; Young *et al*, 2014).

Onion skins are abundantly produced as wastes or by-products from the food processing industry and from almost every kitchen and are thrown away as solid wastes since onion is one of the main vegetables consumed daily, especially in Nigeria. Onion consists mostly of quercetin content and this is the major flavonoid found in red onion skin (Ong & Karim, 2017; Rhim *et al*, 2015). More than a million tons of onion skins are thrown off as waste in the European Union (Benitez *et al*, 2011) and these onion skins are known to contain the highest concentrations of apolyphenolic compound called quercetin and other flavonoids, (Mulazimoglu & Ozkan, 2008; Sayed *et al.*, 2014; Costa *et al.*, 2016).

Flavonoids are a group of compounds contained in onion with high propensity to form chelates because they can undergo ion chelation as a result of their specific chemical structure and they have been known to possess metal-chelating properties (Berlier *et al.*, 2013). They are divided into several classes based on their chemical structures (Symonowicz & Kolanek, 2012) and are spread throughout the plant kingdom (Samanta & Das, 2015). Quercetin is a flavonoid known to have metal-chelating ability as a result of its hydroxyl groups since it is a polyphenol (Mulazimoglu & Ozkan, 2008; Sayed *et al.*, 2014; Masoud *et al*, 2014; Liu & Guo, 2015; Costa

et al., 2016; Yılmaz & Pekin, 2017). Onion is one of the major sources of flavonoids amongst others like apple, tea, citrus fruits, nuts and beverages.

The accumulation of unwanted materials on the surfaces of submerged equipment such as oil pipelines, ship hulls and heat exchangers is a serious problem as it engenders a lot of cost in terms of fuel, maintenance and efficiency of marine vessels. This problem was addressed by the use of tributyltin-based antifouling paints, but because of environmental concerns this was banned and there is therefore the need to develop ecofriendly marine paints from alternative sources such as natural products (Jellali et al., 2013). Several elements have been incorporated in paint formulation before such as cobalt, Nickel, molybdenum or aluminum as additive (Roselli et al., 2017). In this work, we synthesized pigments for marine coating using extract of red onion skin, a flavonoid and azo-metal complexes of copper. This product is expected to be less toxic to the environment than the commercially available products.

2.0 EXPERIMENTAL

Red Onion skins were sourced by peeling the dry skin of red onion bulbs. 2-aminophenol, methanol, acetone, sodium hydroxide, sodium nitrite and Cu (II) salts, all of analytical grade were purchased from Sigma Aldrich. Infra-red spectra were obtained using KBr discs on a Shimadzu 8400S FTIR spectrophotometer in the region of $500\text{-}4000\text{cm}^{-1}$. Ultra violet spectra were carried out using Cary 50 Bio UV Spectrophotometer within the wavelengths of 200-800 nm. Scanning Electron microscopy of the samples was done using SEM. JEOL JXA 6400. The pH was measured using a Consort C531 pH/Conductivity meter while melting points determined using Gallen Kemp melting point apparatus.

2.1 Collection and pretreatment of red onion skin (ROS).

Red onion skins were collected from Fruit Garden market in Port Harcourt, Nigeria. The skins were cleaned and dried. The dried skins were powdered using domestic blender, sieved to a mesh size of $355\mu\text{m}$ and stored in dry, air-tight containers. They were further used in the extraction process following the method according to Manasa et al., (2014) with slight modification.

2.2 Chemical Modification of Red Onion Skin Extract (ROSE)

The red onion skin extract (ROSE) was modified using benzenediazonium chloride, an aromatic diazonium salt. The salt was synthesized by diazotization reaction of 2-aminophenol according to the methods by Myek et al, (2014) and Akaho et al 2018 with slight modification.

2.2.1. Synthesis of the Benzenediazonium salt.

Using the method described by Akaho et al, (2018), 1.09 g (0.01 mol) of 2-aminophenol was dissolved into 45 ml of distilled water. 12 ml of concentrated hydrochloric acid was slowly added while stirring. The resulting solution was cooled in an ice-bath at $0\text{-}5^{\circ}\text{C}$. 0.7g (0.01 mol) of cold NaNO_2 was added drop wise while stirring and maintaining the temperature between $0\text{-}5^{\circ}\text{C}$. After the addition, the reaction mixture was stirred for another 2-3 minutes. The resultant solution was benzenediazonium chloride.

Furthermore, the proposed method for the modification of UROSE with diazonium salt of 2-aminophenol is as reported by Akaho et al., 2018, with the replacement of the carboxyl group with a hydroxyl group of the aromatic amine.

2.2.2. Preparation of modified red onion skin extract of the benzenediazonium salt (APmROSE)

An alkaline solution of ROSE was prepared by dissolving 3.02 g of ROSE into 30 ml of 10% sodium hydroxide solution in a 250 ml beaker. The resulting solution was cooled in ice-bath at 0-5°C. 2-aminophenol modified red onion skin extract (APmROSE) was prepared by slowly adding the benzenediazonium chloride solution to the alkaline solution of red onion skin extract while stirring at 0-5°C. After addition, the reaction mixture was stirred for another 10 to 15 minutes to ensure the reaction goes to completion. The resulting precipitate was filtered using suction filtration apparatus, washed with small amount of cold water and dried at ambient temperature for 3-5 days.

2.2.3 Preparation of metal complex APmROSE

The method of Mishra et al., (2017) was adopted with slight modification. In a two necked round bottom flask equipped with an electromagnetic stirrer and thermometer, 0.84g (0.002 mol) of red onion skin extract modified with salt of 2-aminophenol (APmROSE) was dissolved in 5cm³ of methanol for 10 minutes. The colour of the solution was reddish brown. 0.68g (0.004 mol) of Cu (II) chloride was added quickly in the reaction mixture. The colour of the solution turned to brown. It was stirred for four hours, then filtered and the filtrate evaporated at room temperature. The resulting dark coloured product was washed with methanol and dried in a vacuum desiccator.

3. RESULTS AND DISCUSSION

The result for the physical characterization of UROSE, APmROSE and Cu-APmROSE is as presented in table 1 below.

Table 1: Physical Characterization

Compound	Colour	Melting point/°C	Percentage yield	Soluble in	Insoluble in
UROSE	Red	102-105	10.0	M, E Ac, EA	H, H ₂ O
APmROSE	Brick Red	105-110	72.6	M, E Ac, EA	H, H ₂ O
Cu-APmROSE	Brown	>370	84.9	M, E Ac, EA	H, H ₂ O

Where M=Methanol, E=Ethanol, Ac=Acetone, EA=Ethyl acetate and H=Hexane

From the result, the metal complex had a very high value of greater than 370°C as expected. The high melting point of the metal complex is an indication to its stability to light and heat in an oilfield environment. Its insolubility in water attests to its suitability in marine environment.

Chemical Characterization

Table 2 gives the UV – Visible bands while tables 3 – 5 present data for FT-IR Analysis of UROSE, APmROSE and Cu-APmROSE respectively. Additionally, figures 1 and 2 show results of Scanning Electron Microscopy of UROSE and APmROSE.

Table 2: UV-Visible Results

Compound	$\lambda_{\text{max}}/\text{nm}$
UROSE	397
APmROSE	512
Cu-APmROSE	334

Table 3: Major functional groups present in UROSE

Ligands	Major peaks (cm^{-1})	Functional groups Present
UROSE	3402.54	O-H stretch vibrations for phenols (Ashokkumar&Ramaswamy, 2014; Shama et al, 2014;Yuen et al, 2005)
	2931.90 and 2862.46	Symmetric and assymmetric C-H stretching vibrations of a saturated paraffinic fragment (Coates, 2000; Shama et al.,2014)
	2353.23	CO ₂ in the beam (poor background correction)
	1643.41	C=O stretching vibrations for aromatic ketone (Desai et al, 2007; Jber et al, 2011)
	1504.53	C=C stretch vibrations (Shama et al., 2014; Yuen et al., 2005), while the peak at 1411.94 is due to C-C bond
	1273.06	C-O from alcohol
	1157.33	C-O vibrations due to the presence of C-O-C linkage for ethers or C-O stretching of C-O-H linkage of alcohols(Desai et al., 2007; Nnaji, Okoye, Ezeokonkwo&Ani, 2013) or -C-H bending from aromatic compounds

Table 4: Major functional groups present in APmROSE

Ligand	Major peaks (cm^{-1})	Functional groups present
APmROSE	3433.41	O-H stretch vibrations for phenols (Ashokkumar&Ramaswamy, 2014; Shama et al,2014;Yuen et al, 2005)
	2862.46 and 2924.18	Symmetric and assymmetric C-H stretching vibrations of a saturated paraffinic fragment (Coates, 2000; Shama et al.,2014)
	2353.23	CO ₂ in the beam (poor background correction)
	1643.41	C=O stretching vibrations for aromatic ketone (Desai et al., 2007; Jber et al., 2011)
	1512.24	N=N stretching vibrations (Mohammed &Mustapha, 2010).
	1265.35	Aromatic C-N bond, both from azo compounds (Ahmed et al., 2016; Desai et al., 2007)
	1165.04	C-O vibrations due to the presence of C-O-C linkage for ethers or C-O stretching of C-O-H linkage of alcohols(Desai et al., 2007; Nnaji et al., 2013) or -C-H bending from aromatic compounds
	794.70	1,3-disubstituted benzene ring (Coates, 2000)

Table 5: Major functional groups present in Cu-APmROSE

Ligand	Major peaks (cm ⁻¹)	Functional groups present
Cu-APmROSE	3448.84	O-H stretch vibrations for phenols (Ashokkumar&Ramaswamy, 2014; Shama et al.,2014;Yuen et al.,2005)
	2956.97 and 2848.96	Symmetric and asymmetric C-H stretching vibrations of a saturated paraffinic fragment (Coates, 2000; Shama et al.,2014)
	2335.87	CO ₂ in the beam (poor background correction)
	1616.4	C=O stretching vibrations for aromatic ketone (Desai et al., 2007; Jber et al., 2011)
	1458.23	N=N stretching vibrations (Mohammed &Mustapha, 2010).
	1288.49	Aromatic C-N bond, both from azo compounds (Ahmed et al., 2016; Desai et al., 2007)
	1153.47	C-O vibrations due to the presence of C-O-C linkage for ethers or C-O stretching of C-O-H linkage of alcohols(Desai et al., 2007; Nnaji et al., 2013) or -C-H bending from aromatic compounds
	798.56	1,3-disubstituted benzene ring (Coates, 2000)

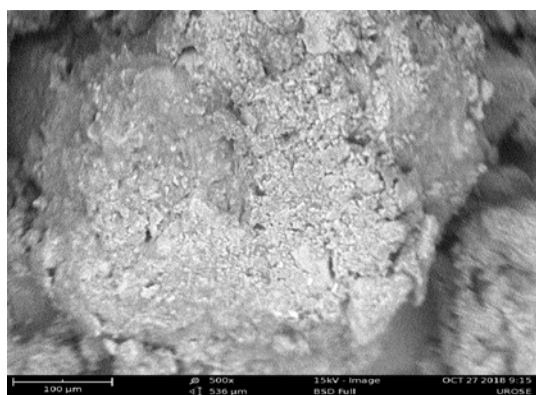


Figure 1: Scanning Electron Microscopy of UROSE

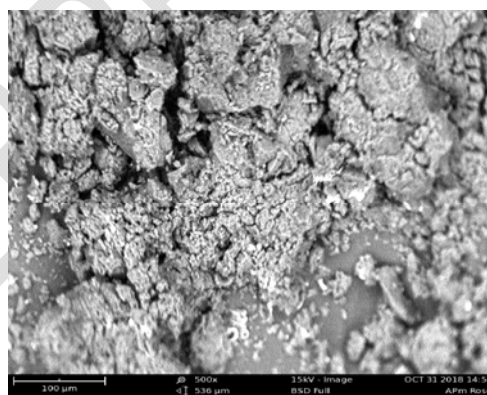


Figure 2: Scanning Electron Microscopy of APmROSE

The UV-Visible results are an indication of the different electronic transitions that took place in the different compounds. The appearance of the azo band (1450-1600cm⁻¹) confirmed the presence of the azo group (N=N) in the azo compound and in its metal complex(Ali & Zahra, 2011). Tables 4 and 5 are the FTIR results of APmROSE and Cu-APmROSE. The IR spectra showed the value of N=N stretching frequency for APmROSE to be 1521.24cm⁻¹ with an area of 18.203 while Cu-APmROSE has stretching frequency at 1458.23cm⁻¹ with an area of 12.9932. This is an indication of the involvement of the N=N bond in coordination to the metal. The O-H stretching frequency increased from 3402.54cm⁻¹ in UROSE with an area of 300.428 to 3433.41cm⁻¹ in APmROSE and 3448.84 cm⁻¹ in Cu-APmROSE. Change in the position of O-H shows that it is involved in coordination between the azo compound and its metal complex (Ali & Zahra, 2011). The FTIR shows that N=N and N=C bonds are present in the azo compound and in its metal complex. Figures 5 and 6 present the SEM photograph of the Unmodified onion

skin extract and modified onion skin extract with 2-aminophenol. The different morphology is an indication of formation of a new compound.

4.0 Conclusion

We were able to formulate an azo compound by coupling diazotized 2-aminophenol with red onion skin extract which has quercetin as its major constituent. Its Cu(II) complex was also synthesized. They were characterized using FTIR and UV-Visible spectrophotometers. It is on the basis of the FTIR results that the structures of the compound and metal complex were proposed. We are basing our conclusion of our results to propose the use of this pigment for the formulation of surface coating for use in marine environment. We expect this product to be more environmental friendly compared to the formulations using tributyltin, cobalt and chromium.

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